CHANGE IN THE ASSOCIATED MOLECULAR STRUCTURE OF COALS IN PYRIDINE/CS2 MIXED SOLVENTS.

H.Kumagai, K.Matuoka, K.Norinaga T.Chiba,
Center for Advanced Research of Energy Technology, Hokkaido
University,
Kita-ku, Sapporo 060, Japan,

M.Sasaki,
Hokkaido National Industrial Research Institute,
Toyohira-ku, Sapporo 062, Japan

ABSTRACT

In order to evaluate noncovalent interactions in coal, change in the associated molecular structure of coals in pyridine/CS_2 mixed solvents have been investigated. For bituminous coal, variation in L-band EPR spectra with mixing ratio of the solvents is in a close correspondence to that in equilibrium swelling ratio and in molecular mobility obtained from ^{1}H-NMR. The EPR spectra for lignite show similar variation to that for bituminous coal, however, does not correlate with equilibrium swelling ratio and molecular mobility. Since the L-band EPR characteristics appear to reflect the situation of aromatic π-π and charge transfer interactions in coal, these results indicate that swelling in the mixed solvents proceed with the declining of non-covalent interaction, such as aromatic π-π and charge transfer interaction, in coal.

INTRODUCTION

The chemical and physical properties of coal are affected not only with the chemical structure of coal molecules, but also with the associated molecular structure. Coal is believed to be complex macromolecular compounds containing several types of noncovalent interactions, such as hydrogen bonding, van der Waals, charge transfer and aromatic π-π interaction. The type and strength of noncovalent interactions existing in coal have been postulated to govern the associated molecular structure. Since the noncovalent interactions play an important role in the physical and chemical properties of coal, it has become of general interest in recent years.

Larsen and Kovac [1,2] have proposed two components (phase) coal structure model, in which coal consists of two components, i.e., a covalently cross-linked macromolecular network component (MM phase) and a low molecular weight component (M phase) trapped noncovalently inside the network. Based on the two components coal structure model, Marzec and co-worker [3,4] have attempted to elucidate the extraction mechanism of bituminous coal with electron-donor-acceptor interaction between M phase in the coal and solvents. The contribution of noncovalent interactions to cross-linked structure was also suggested from coal swelling and extraction studies [5,6]. While, it was argued that such noncovalent interactions are too weak to from and stabilize the cross-linking structure which affects swelling behaviour of coal [7].

Mixed solvent systems, such as NMP/CS_2 and pyridine/CS_2 have a high potential to get large amount of extracts from many bituminous coals at room temperature [8,9]. Iino and Takanohashi have indicated that no significant reaction between coal and the solvent, which results in an increase of the extraction yields, occur for this extraction [8]. In spite of the extensive studies of swelling and extractability of coal with the mixed solvent systems [10-12], the mechanism of coal extraction and swelling with the mixed solvent systems has not been clarified in detail.

In this psper, in order to evaluate the effects of noncovalent interactions on the associated molecular structure of coals, swelling behaviour of coals in the mixed solvents has been investigated by means of 1H-NMR relaxation time and L-band EPR spectroscopy. EPR spectroscopy is one of the useful techniques to investigate noncovalent interactions such as aromatic π-π and charge transfer interaction. X-band EPR is, however, not allowed to measure the spectrum of sample in solvents with high permittivity. Thus, we have attempted to build L-band EPR from which favorable results are provided. Measurement L-band EPR for swelling and extraction of coal

may bring deep information about noncovalent interaction in coals.

EXPERIMENTAL SECTION
Coal Samples and Reagents.
Upper Freeport bituminous coal (UF) and Beulah Zap lignite (BZ) were selected from Argonne Premium coal samples and used in this study. Pyridine-d5 and CS2 (G.R. grade) for solvent were used without further purification.

Sample Preparation.
Coal sample was dried under a vacuum at 40°C for 24 hours. The dried coal sample was placed in glass sample tube (10mm o.d.). The initial height (h1) of the coal particle bed was measured by a caliper. The mixed solvent was then poured into the sample tube. The coal suspension was standing for 7 days under nitrogen atmosphere. Swollen coal bed height (h2) was measured prior to the EPR and NMR measurement. Equilibrium swelling ratio was expressed as the ratio of h2 and h1.

^{1}H-NMR Measurement.
Spin-spin relaxation time (T_2) of the swollen coal sample was measured with JEOL JNM-Mu25 spectrometer (25MHz) employing solid-echo (90°x-τ-90°y) pulse sequence at 20°C under nitrogen atmosphere.

L-band EPR Measurement.
L-band EPR spectra were monitored with a Varian E-109 EPR spectrometer equipped with Micro Device Co.Ltd. MWG-2L L-band microwave bridge and MSC-2LG loop-gap resonator. In order to get the high signal sensitivity, 10mm (o.d.) sample tube was used. The effective portion of sample tube to be irradiated with microwave is 22mm. L-band EPR measurement was carried out at 20°C under nitrogen atmosphere. Spectral intensities of coals in the mixed solvents were corrected by the effects of dielectric characteristics (permittivity) of solvents and density decrease of coal particles due to swelling.

RESULTS AND DISCUSSION
Equilibrium Swelling Ratio
The equilibrium swelling ratio of UF and BZ in the mixed solvents are shown in Figure 1 and 2 as a function of mixing ratio of pyridine and CS2 (pyridine vol%). The swelling ratio of UF increases with the fraction of pyridine and reaches a maximum value at about 50vol% pyridine. Then, the swelling ratio decreases with the increase in pyridine vol%. For BZ, the swelling ratio increases with increase in pyridine vol%, and show maximum value at about 80-100vol% pyridine. These results suggest that the swelling characteristics, i.e., change in the equilibrium swelling ratio with mixing ratio, is dependent on the chemical and associated structure of coal molecules. Since the swelling of coal in polar solvents is results from declining of noncovalent interactions in coal [13], the difference of the swelling characteristics with mixing ratio of the solvent appear to be reflecting the type and strength of noncovalent interactions existing in the coals.

^{1}H-NMR Relaxation Time.
The solid-echo signals obtained from coal in the mixed solvents contained two components, namely the relatively slowly relaxing tail of the signals and rapidly decaying signals. The former can be attributed to the hydrogen in mobile molecular structures, and later can be attributed to the hydrogen in rigid-like (immobile) molecular structure. The variations of T_2 values for two components of UF and BZ are plotted as a function of pyridine vol% in Figure 3 and 4, respectively. For UF, T_2 for mobile structures (T_2m) increases with increase in pyridine vol% in the mixed solvent and reaches a maximum value at about 50vol% pyridine. T_2 for immobile structures (T_2im) remains almost constant value with increase in pyridine vol%. The T_2m for BZ increases monotonously with increase in pyridine vol%.

The separation of the solid-echo signals permits hydrogen-weighted mobile and immobile fractions of the molecular structure in coal. The distribution of the mobile and immobile fractions for UF and BZ are shown in Figure 5 and 6. Variations in the fraction of mobile components for both UF and BZ are well correlated with the variation of T_2m. The ^{1}H-NMR relaxation characteristics described above are in a close correspondence with swelling characteristics. The spin-spin relaxation time and the fraction of mobile components

vary in proportion to equilibrium swelling ratio. The enhancement of molecular mobility due to solvent induced swelling may result the ^{1}H-NMR relaxation characteristics.

L-band EPR spectroscopy.

The intensity of EPR spectra for UF coal decrease with increase in the mixing ratio of pyridine. It is noted that the intensities decrease at the mixing ratio from 0 to 50% and reach a minimum in the vicinity of 50 vol% of pyridine. The EPR characteristics for UF in the mixed solvents reflect the swelling behaviour of coal. For BZ, the characteristics are almost similar to those of UF, but independent of the swelling behaviour.

The EPR spectra for UF and BZ consist two components, one broad (BC) and one narrow (NC) components. Variations in the components with pyridine vol% in the mixed solvents are shown in Figure 7 and 8. It can be clearly seem that the narrow components for both UF and BZ do not change with pyridine vol%, while the broad components show minimum values at pyridine 50vol%. With EPR spectroscopy, not only stable free radical, but also the sifted and transferred electrons can be detected. The swelling in the mixed solvents proceed without significant reaction between coal and the solvents [8]. Therefore, variation in the intensities for BC might be due to disappearance of the sifted and transferred electrons result from declining of noncovalent interactions, such as aromatic π-π and charge transfer interactions.

CONCLUSIONS

1. L-band EPR characteristics are considered to have a close relation to the aromatic π-π and charge transfer interaction in coals.
2. The molecular mobility of coals obtained from 1H-NMR vary in proportion to swelling behaviours.
3. For UF, L-band EPR characteristics are well correlated with swelling behaviour and molecular mobility, indicating that the associated structure of UF is affected strongly with the aromatic π-π and charge transfer interactions.
4. For BZ, the characteristics are almost similar to those of UF, and independent of the swelling behaviour and molecular mobility. These facts indicate that the interaction is much less effective for the associated structure of BZ than that for UF.

REFERENCE

(1) Larsen,J.M.;Kovac,J. In *Organic Chemistry of Coal*; Larsen,J.W.,Eds.;ACS
    Symposium Series 71;American Chemical Society:Washington,DC,1981;43
(2) Kovac,J.;Larsen,J.W. *Prepr.Am.Chem.Soc.,Div.Fuel Chem.* 1975,*20(2)*,122
(3) Marzec,A.;Juzwa,M.;Betlej,K.;Sobkowiak,M. *Fuel Processing Technology* 1979, 2,35
(4) Marzec,A. *Proc. Symposium on Chemistry of Coal Liquefaction and Catalyst*;
    Hokkaido Univ.:Sapporo,Japan,1985,42
(5) Nishioka,M. *Fuel* 1972,71,941
(6) Fujikawa,M.;Ohsuga,H.;Takanohashi,T.;Iino,M. *Energy Fuels* 1992,*6*,859
(7) Painter,P. *Energy & Fuels* 1992,*6*,863
(8) Iino,M.;Takanohashi,T.;Ohsuga,H.;Toda,K. *Fuel* 1988,*67*,1639
(9) Iino,M.;Takanohashi,T.;Ohsuga,H.;Tsueta,H.;Sanokawa,Y. *Fuel* 1989,*68*,1588
(10) Ishizuka,T.;Takanohashi,T.;Ito,O.;Iino,M. *Fuel* 1993,*72*,579
(11) Liu,H.-T.;Ishizuka,T.;Takanohashi,T.;Iino,M. *Energy Fuels* 1993,7,1108
(12) Yun,Y.;Suuberg,E.M. *Fuel* 1993,72,1245
(13) Larsen,J.W.;Green,T.K.;Kovac,J. *j.Org.Chem.* 1985,*50*,4729-4735
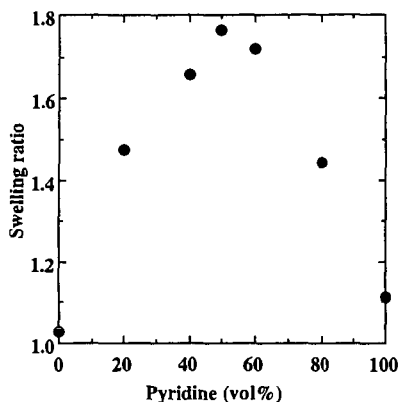
Figure 1. Change in equilibrium swelling ratio for UF with pyridine vol.% in mixed solvent
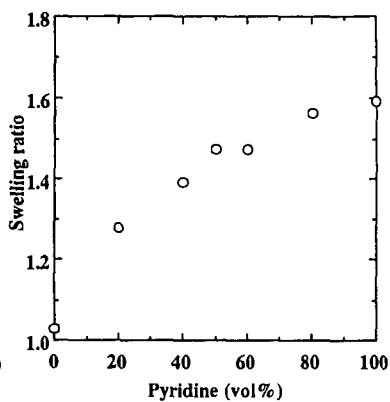

Figure 2. Change in equilibrium swelling ratio for BZ with pyridine vol.% in mixed solvent
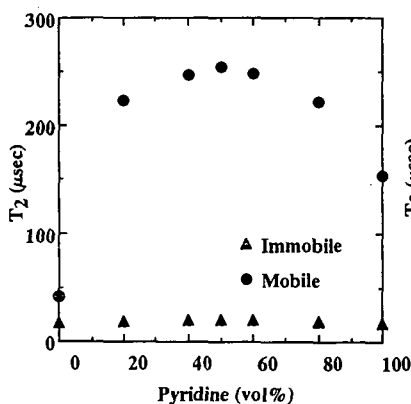

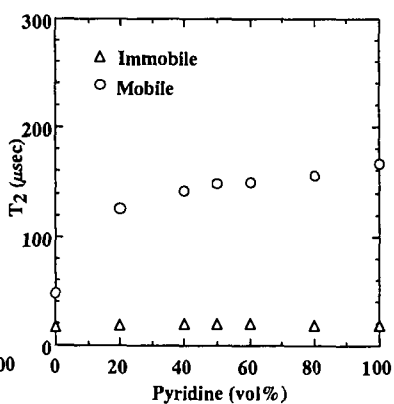**Figure 3.** Effects of pyridine vol% in mixed solvent on spin-spin relaxation time, T_2, for UF

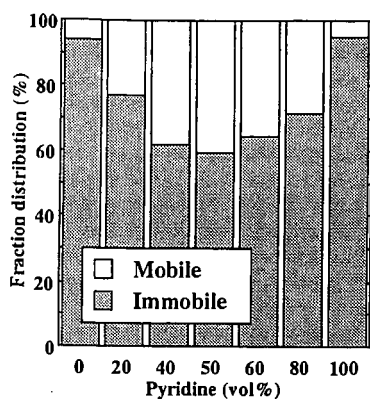**Figure 4.** Effects of pyridine vol% in mixed solvent on spin-spin relaxation time, T_2, for BZ

Figure 5. Distribution of mobil and immobile fractions for UF in mixed solvent
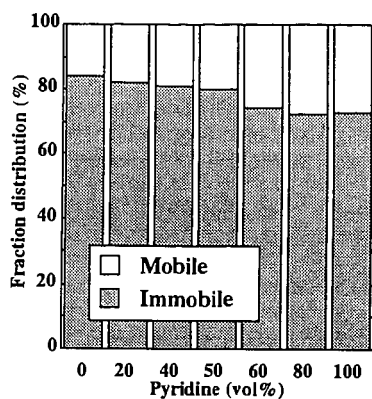

Figure 6. Distribution of mobil and immobile fractions for BZ in mixed solvent
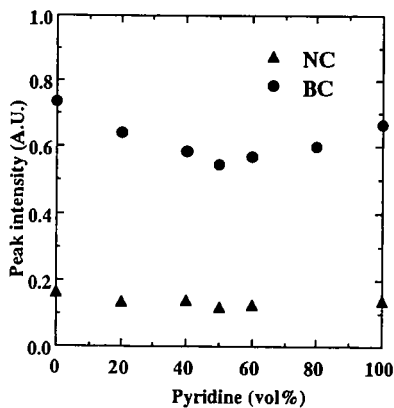

Figure 7. Change in the peak intensity of NC and BC for UF with pyridine vol% in mixed solvent
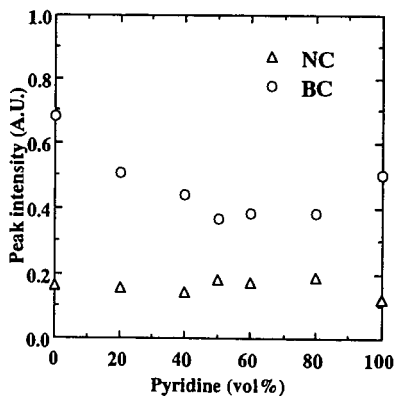

Figure 8. Change in the peak intensity of NC and BC for BZ with pyridine vol% in mixed solvent